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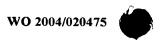
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AMENDED CLAIMS

[received by the International Bureau on 03 January 2004 (03.01.04); original claims 1-2-6-7-8 amended; original claim 3 replaced by new claim 3; original claim 4 cancelled; remaining claims unchanged (3 pages)]

What is claimed is:

1. A functional polymer that is defined by the formula

 π -R1- α

where π is a polymer chain, R^1 is a bond or a divalent organic group, and α is a sulfur-containing heterocycle selected from a thiirane, thietane, thiolane, thiazoline, dihydrothiophene, thiadiazine, thioxanthene, thianthrene, phenoxathiin, dihydroisothiazole, or thienofuran group or substituted form thereof.

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2. A method for preparing a functional polymer, the method comprising: terminating a living polymer chain with a functionalizing agent where the functionalizing agent is defined by the formula

 $Z-R4-\alpha$

where Z is a leaving group or an addition group, R^4 is a bond or a divalent organic group, and α is a sulfur-containing heterocycle selected from a thiirane, thietane, thiolane, thiazoline, dihydrothiophene, thiadiazine, thioxanthene, thianthrene, phenoxathiin, dihydroisothiazole, or thienofuran group or substituted form thereof.

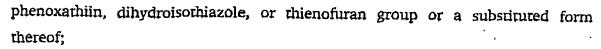
3. A method for preparing a cured tire component, the method comprising: providing a rubber formulation comprising at least one vulcanizable rubber and a filler, where the at least one vulcanizable rubber is a functional polymer that is defined by the formula

 π -R 1 - α

where π is a polymer chain, R^1 is a bond or a divalent organic group, and α is a sulfur-containing heterocycle selected from a thirane, thietane, thiolane, thiazoline, dihydrothiophene, thiadiazine, thioxanthene, thianthrene,

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forming the rubber formulation into a green tire component; vulcanizing the green tire component to form a cured tire component.

4. The polymer of claim 1, or the method of claim 3, where the functional polymer can be defined by the formula

$$\pi \xrightarrow{R^1} \xrightarrow{S} \xrightarrow{R^2} R^3$$

where π is a polymer chain, R^1 is a bond or a divalent organic group, each R^2 is independently hydrogen or a monovalent organic group, each R^3 is independently hydrogen or a monovalent organic group, or where each R^3 combine with each other to form a divalent organic group; or where the functional polymer can be defined by the formula

$$\begin{array}{c}
OR^5 \\
\pi - Si - R^6 - \alpha
\end{array}$$
 $\begin{array}{c}
OR^5
\end{array}$

where π is a polymer chain, each R^5 is independently a monovalent organic group, R^6 is a bond or a divalent organic group, and α is a sulfur-containing heterocycle.

5. The polymer of claim 1, or the method of claim 3, where R¹ includes the residue of an addition reaction between an addition group and a living polymer, and wherein the addition group comprises a nitrile group, a Schiff base, a ketone group, an aldehyde group, or an ester group.

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- 6. The polymer of claim 1, or the method of claim 2 or 3, where the polymer chain is a rubbery polymer having a Tg that is less than 0°C.
- 7. The polymer of claim 1, or the method of claim 2 or 3, where the polymer chain is polybutadiene, polyisoprene, poly(styrene-co-butadiene), poly(styrene-co-butadiene-co-isoprene), poly(isoprene-co-styrene), or poly(butadiene-co-isoprene).
- 8. The method of claim 2, where Z comprises a halide, a thio alkoxide group, an alkoxide group, a dialkyl amine group, a nitrile group, a Schiff base, a ketone group, an aldehyde group, or an ester group.
 - 9. The method of claim 3, where the filler is carbon black, silica or both.

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A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08C19/44 C08F8/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08CC08C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the re	elevant passages	Relevant to claim No.
х	EP 1 099 711 A (JSR CORP; BRIDG CORP (JP)) 16 May 2001 (2001-05- abstract; claims; examples 1,2; page 6, line 40 - page 7, line 1	·16) table 1a	1-10
X	DE 19 01 900 A (INTERNAT SYNTHET COMP) 11 September 1969 (1969-09 claims; example 8 page 7, paragraph 2 - page 8, pa	1–11)	1,2,4,5, 7,9
X	EP 0 693 505 A (BRIDGESTONE CORP 24 January 1996 (1996-01-24) abstract; claims page 4, line 1 - line 2)	1,3,4,6, 7,10
X	US 2 515 318 A (SCHOENE DWIGHT L 18 July 1950 (1950-07-18) claims; examples) -/	1,3-8,10
<u> </u>	ner documents are listed in the continuation of box C.	X Patent family members are listed	in annex.
'A' docume consid 'E' earlier of filing d 'L' docume which idation 'O' docume other r 'P' docume later th	nt which may throw doubts on priority claim(s) or is cited to establish the publication date of another n or other special reason (as specified) and referring to an oral disclosure, use, exhibition or	 'T' later document published after the interest or priority date and not in conflict with clied to understand the principle or the invention 'X' document of particular relevance; the cannot be considered novel or cannot involve an inventive step when the document of particular relevance; the cannot be considered to involve an involve an inventive step when the document is combined with one or moments, such combined with one or moments, such combination being obvious in the art. '&' document member of the same patent to the same patent of the same patent to the same pat	the application but sory underlying the laimed invention be considered to current is taken alone laimed invention rentive step when the re other such docusis to a person skilled laimity
	5 December 2003	Date of mailing of the international sea	rch report
Name and m	nailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Mettler, R-M	



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	ation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Rel	evant to claim No.
A	EP 0 295 675 A (BASF AG) 21 December 1988 (1988-12-21) abstract; claims; examples		1-10
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Form PCT/ISA/210 (continuation of second sheet) (July 1992)



International Application No PCT/US 03/27081

Patent document cited in search report	Į	Publication date		Patent family member(s)	Publication date
EP 1099711	Α	16-05-2001	JP JP EP	2001139634 A 2002030110 A 1099711 A2	22-05-2001 31-01-2002 16-05-2001
DE 1901900	A	11-09-1969	DE GB	1901900 A1 1258893 A	11-09-1969 30-12-1971
EP 0693505	A	24-01-1996	CA DE DE EP ES JP	2153946 A1 69509448 D1 69509448 T2 0693505 A1 2132467 T3 8048707 A	19-01-1996 10-06-1999 02-09-1999 24-01-1996 16-08-1999 20-02-1996
US 2515318	A	18-07-1950	GB	609467 A	30-09-1948
EP 0295675	A	21-12-1988	DE DE EP JP US	3720322 A1 3866029 D1 0295675 A2 1016801 A 4839434 A	29-12-1988 12-12-1991 21-12-1988 20-01-1989 13-06-1989